Chapter 1

A brief history of the lighting devices, needs/ uses of new phosphor materials and various characterization techniques used in the present work are discussed in this chapter. The history of lighting devices explains different types of lighting devices, their advantages and disadvantages. The importance and applications of rare earth based phosphor materials are also discussed. The basic characteristics of rare earth elements show its application in the solid state lighting devices. Solid state reaction method, the method of preparation of the phosphor samples, along with the structural properties of Sr$_{1-x}$Ca$_x$TiO$_3$ is also discussed. Different characterization techniques like XRD, EDS, FTIR, SEM, UV-Vis-NIR spectroscopy, Photoluminescence emission and excitation etc. are described. Discussion on optical spectral characterizations like JO intensity analysis, radiative properties, luminescence decay analysis, CIE color coordinates etc. is included in this chapter. Essential theory of dielectric spectroscopy is also explained in this chapter.
Chapter 1

General Introduction & Characterization Techniques

1.1 Introduction

In the world of lighting, it was the age of incandescent light bulbs for the past hundred years. Then the Compact Fluorescent Lamps (CFLs) replaced incandescent lamps because of its high efficiency over incandescent lamps. Initially, CFLs had many drawbacks such as they were very expensive, the light they emitted was cold and their brightness decreased over time. But recently CFLs improved significantly with reduced cost, improvement in Color Rendering Index (CRI), producing warmer white light with CRI up to 90, increased efficiency etc. However, commonly used fluorescent lamps use mercury, which is highly toxic and harmful to the environment and generates ultraviolet photons. In order to reduce the use of mercury in lighting devices, there is a need for continuous research on inorganic Light Emitting Diodes (LEDs) and phosphor materials. The technological and research interest of phosphor materials have been significantly increased since the first phosphor, barium sulfide, was produced by Vencenzio Cascariolo in 1603 [1]. Since then phosphor materials have been widely used for different applications and an active area of research for various applications. At present solid state lighting technology based on phosphor-converted White Light Emitting Diodes (pc-WLEDs) dominates the lighting applications. So the search for new phosphor materials with high efficiency and good color rendering
properties is actively going on. A short history of lighting technology is
given in the following sections:

1.1.1 Incandescent Lamp

While Thomas Alva Edison is considered to be the inventor of the
incandescent light bulb in 1879, there were a number of people who
worked and invented components before him. In 1802, Sir Humphry Davy
discovered incandescence in a platinum wire. Later in 1841, Frederick de
Moleyns patented an incandescent lamp within a glass bulb with a partial
vacuum. But before Edison, in 1860, Sir Joseph Swan obtained a UK patent
for a carbon filament incandescent lamp operating in a partial vacuum. In
1879, Thomas Edison patented a more efficient version of Swan’s invention,
with an improved vacuum. Later, in 1902, Werner von Bolton discovered
tantalum filaments with increased efficiency, durability and lifetime. In
1904, Alexander Just and Franz Hanaman patented a sintered tungsten
filament, a step towards the modern bulb. Further improvements followed
the use of inert gas, coiled filament, silica coating on the inside of the bulb
etc.

Incandescent bulbs are the second most used lamp in the world
today behind fluorescent lamps. An incandescent bulb uses electricity to
heat the coiled tungsten filament in an evacuated glass tube, resulting in
radiating white light. They have some advantages such as low cost, best
possible CRI (approaching 100) and carry no toxic materials like mercury,
alloys or semiconductors. The spectrum of radiation emitted by the
incandescent bulb is very broad, the entire wavelength range (400-700 nm)
of visible light. But the major disadvantage is only about 10% of the input
electrical energy is converted to visible light and the rest 90% of energy is
emitted as heat. So it is not energy efficient solution for lighting devices. The lifetime of an incandescent bulb is typically 1000 hrs with luminous efficacy typically 4-18 lm/W.

1.1.2 Fluorescent Lamp

The first commercial fluorescent lamp was made by General Electric scientists in 1938. Fluorescent tubes are made of a glass tube filled with inert gas and a small amount of mercury vapour. The electric current between the electrodes at each end of the glass tube excites the electrons in the mercury vapour. These excited electrons emit photons in the UV frequencies. The UV light is then converted into visible light by using a phosphor coating on the inner surface of the glass tube. Fluorescent tubes have reasonable cost and longer lifetime (7000-15000 hrs) comparable to the incandescent bulbs. They have very high luminous efficacy (60-105 lm/W) and good Color Rendering Index values. They produce even and glare-free light distribution. These advantages made fluorescent lamps to rapidly replace the incandescent lamps.

1.1.3 Compact Fluorescent Lamp

In 1976, Edward E Hammer, an engineer at General Electric, invented spiral Compact Fluorescent Lamps (CFLs). CFLs consist of argon and mercury vapour filled in a straight or spiral shaped glass tube coated with fluorescent material. They also consist of an integrated ballast to produce electric current. Their luminous efficacy is 35-80 lm/W with a lifetime of 6000-15000 hrs. But the lifetime of CFL depends on how it is used i.e. the long lifetime is achieved only if the lamp is left on for longer periods of time. The short duration use decreases the lifetime of CFLs. The compact fluorescent lamps were widely used for lighting applications. But
it has a major environmental drawback. Each CFL contains about 5 mg of mercury which is a highly toxic heavy metal. Since then many studies pointed out the necessity of mercury free lighting devices and more importantly, the need for solid state lighting devices.

1.1.4 Solid State Lighting

Solid state lighting technology is considered as the third revolution of the lighting industry followed by incandescent lamps and fluorescent lamps. The first solid state light source was demonstrated by Henry J. Round in 1907 [2]. We can control the spectral power distribution, spatial distribution, polarization properties and color temperature of solid state light sources [3-5]. So they have a wide range of applications like traffic signals, signboards, street lighting, general illumination, backlighting, laptop displays, flashlights, imaging, plant growing and medical treatment [5-11]. It is the lighting technology that uses Light Emitting Diode (LED) as the source of illumination rather than electric filaments or gases. Light Emitting Diode, a semiconductor light source, has a p-n junction diode which emits light on applying voltage. When a suitable voltage is applied to the leads, the electron-hole recombination occurs by releasing energy in the form of photons. This is known as electroluminescence. The color of the light produced will depend on the band gap of the semiconductor material. LEDs have many advantages such as longer lifetime typically 30000-50000 hrs, environment friendliness (no mercury), large energy savings, better quality output with minimum ultraviolet and infrared radiation, low operating voltage, compact size, ease of control and reduction of greenhouse gases [6, 8, 12]. They also have a luminous efficacy of 60-188
Mainly there are two types of LEDs- Organic LEDs and Inorganic LEDs.

**1.1.4.1 Organic LEDs**

Organic LEDs are made from organic (carbon-based) materials. The structure of organic LED (OLED) contains a cathode, to inject electrons, an emissive layer and an anode, which collects electrons. The OLEDs include large molecule OLEDs (Polymer-based OLEDs) and small molecule OLEDs. All commercial OLEDs are small molecule based since they have higher efficiency and lifetime compared to Polymer-based OLEDs. The organic light emitting materials were first demonstrated in 1963 by Martin Pope and his co-workers at the New York University [13]. But in 1987, Ching W Ting and Steven Van Slyke at Eastman Kodak reported the first organic diode with reduced operating voltage and improvements in efficiency. But it is not yet possible to achieve high brightness along with high efficient OLEDs.

**1.1.4.2 Inorganic LEDs**

Inorganic Light Emitting Diodes are generally called LEDs. The first visible light LED was developed by Nick Holonyak in 1962 [14]. He used Gallium Arsenide Phosphide as the substrate for the diode to produce red light. His former graduate student George M Craford invented the first yellow LED and improved the brightness of red LED in 1972. Thomas P Pearsall developed high brightness LEDs for use with fiber optics in telecommunications in 1976. Later, in 1993 Shuji Nakamura invented the first blue LED using gallium nitride [15].
Even though white OLED is not yet commercially available there are various ways of obtaining white light from inorganic LEDs. One of the current strategies to produce white light with reasonable color rendering properties is to add one or more phosphor materials that emit photons in the visible spectrum by absorbing photons from a narrow band LED. Depending on the properties of phosphor material used, it is possible to adjust the chromaticity coordinates with improved color rendering characteristics [16]. The white LEDs have good luminous efficacy compared to other lighting devices and are free from mercury.

The first commercially available white LED was made of blue LED (InGaN) excited cerium doped yttrium aluminium garnet (YAG) phosphor [17]. The yellow light produced from the YAG phosphor material combined with blue LED gives cool white light. In this case, the LED chip and phosphor material used are nontoxic. Large display screens, interior lighting in cars, buses, trains and planes, exterior lighting on buildings, front bicycle lights etc. uses white LED produced from blue LED converted with a yellow phosphor [12]. But the lack of red light component reduces
the color rendering index of the white light, which is a major disadvantage [18]. The combination of red, green and blue LEDs can also produce cool white light [19]. But the efficiency of green LED is very much less than that of red and blue LEDs, leads to the overall decrease in the efficiency. Also the efficiencies of red, green and blue LEDs change over time thus the quality of white light degrades [12]. They have the poor color rendering and less cost effective for its general use [20-21].

Fig.1.2 Schematic diagram of (a) pc- LED and (b) Blue LED + Yellow phosphor.

By using phosphor-converted white LEDs (pc- WLEDs) we can solve these disadvantages of single/multi LED chip produced white light. Fig.1.2 (a) and (b) represents the schematic diagram of a typical phosphor-converted LED and blue LED + yellow phosphor. Phosphor-converted white LEDs shows the characteristics of high efficiency, long lifetime and energy saving [12]. Mainly the near UV excited blue, green and red phosphor materials produce warm white light with high color rendering properties [22]. Single or multiple phosphor materials can be used to produce white light. But the multiple phosphors based white LEDs have high color rendering index and tunable color temperature [12]. Thus, for
phosphor-converted white LEDs, phosphor materials play an important role by down conversion process. As a result, down conversion phosphors got more importance in the white LED applications. For this purpose novel white, red, green and blue emitting phosphor materials should be needed. As a contribution to the novel phosphor materials, in the present work, we have concentrated on Sr and Ca based new oxide phosphor materials emitting red, yellow and white lights.

1.2 Phosphors

Phosphors are solid luminescent materials that convert energy into electromagnetic radiation, usually in the visible region. In other words, phosphors are the materials that emit photons when excited by an external energy source. This emission of light is termed as luminescence, originated from the latin word “Luminis” means light. Generally, luminescence can be divided into two: fluorescence and phosphorescence. The word fluorescence came from the Latin word, “fluor” means flow and phosphorescence from the Greek words, “phos” (means light) and “phoros” (means carrying). In terms of decay time, we can define Fluorescence and Phosphorescence as for fluorescence the decay time is less than 10 ms (usually ≈ 10⁻⁸ to 10⁻⁹ s) and for phosphorescence the decay time is greater than 0.1 s (usually 0.1 s to few hours). Fluorescence is very fast with a spin allowed transition (Δs = 0) whereas phosphorescence is very slow with a spin-forbidden transition (Δs = 1). However in terms of modern usage, light emission from a material during the time it is exposed to exciting radiation is termed as fluorescence, while the emission after the excitation ceased off is termed as phosphorescence.
Simply, phosphors emit energy from an excited electron as light. This excitation of an electron can be caused by absorption of energy from an external source such as another electron, a photon or an electric field. An excited electron occupies a quantum state whose energy is above the minimum energy ground state. In the case of solids, semiconductors and insulators, the electronic ground state is referred to the levels in the valence band, which is completely filled with electrons. The excited quantum state often lies in the conduction band, which is empty and separated from the valence band by an energy band gap. So a minimum energy equal to the bandgap energy is necessary to excite an electron in a semiconductor or insulator, and the energy released during the de-excitation of the electrons is often nearly equal to the band gap. Under normal conditions, electrons are forbidden to have energies between the valence band and the conduction band. During the de-excitation process electrons loses the excess energy before coming to rest at the lowest energy in the conduction band. This excess energy in the form of photons is termed as luminescence. On the basis of excitation nature luminescence can be further classified as follows:

**Photoluminescence**: Photoluminescence is the spontaneous light emission from any form of matter under optical excitation. Usually, emission is observed by the excitation with electromagnetic radiation often Ultra-Violet, visible light or infrared. The fluorescent lamps for the household and general lighting devices are based on photoluminescence.

**Electroluminescence**: It is the luminescence caused by electric current or a strong electric field. There is another type of electroluminescence known as injection luminescence. Here the electrons are injected from an external supply across a p-n junction. On applying a direct voltage across the
junction, such that the electrons flow to the p region, luminescence is produced by electron-hole recombination in that region. LEDs, which are commonly used for display and lighting applications are based on this principle. Electroluminescent devices are fabricated using organic or inorganic electroluminescent materials. Generally, semiconductors of wide band gap are used as active materials in order to allow the exit of the light. Powder phosphor based electroluminescent panels are frequently used as backlights in liquid crystal displays.

**X-ray luminescence:** It is the luminescence from materials which absorb x-rays and converts the absorbed energy efficiently into UV or visible emission.

**Cathodoluminescence:** It is an optical and electromagnetic phenomenon in which a beam of electrons impact on a luminescent material such as a phosphor, causing the emission of photons in the visible spectrum. The familiar example is the TV screen that uses a cathode ray tube (CRT). It is the reverse process of the photoelectric effect, in which electron emission is induced by irradiation with photons.

**Radioluminescence:** It is the phenomenon by which light is produced in a material by the bombardment of ionized radiation such as beta particles. In radioluminescent light sources, a radioactive substance is mixed with phosphor materials to produce light of a particular color. Radioluminescence can see around high power radiation sources like nuclear reactors and radioisotopes. It is used as light source for night illumination, sign boards or other applications where light must be produced for long periods without external energy sources.
**Mechanoluminescence**: It is also known as triboluminescence or fractoluminescence. An inorganic and organic material subjected to mechanical stress emits light is called mechanoluminescence. It has been observed that all piezoelectric crystals exhibit triboluminescence. The spectra of mechanoluminescence are similar to those of photoluminescence in many substances.

**Chemiluminescence**: It is the luminescence where the energy is supplied by chemical reactions. But not all the chemical molecules are capable of luminescence. Oxidation of white phosphorous in the air is the best-known example of chemiluminescence.

**Bioluminescence**: Luminescence caused by chemical reactions in living things is a form of chemiluminescence. Biochemical reactions inside the cells of some living organisms produce electronic excited states of the biomolecules, which results in luminescence. Fireflies, some bacterias and fungi, angelfish, many sea creatures etc. are the examples of luminescence living things.

**Thermoluminescence**: It is the re-emission of previously absorbed electromagnetic or other ionizing radiation, from certain crystalline materials such as minerals upon heating. This phenomenon has been applied in thermoluminescent dosimeter for dating application.

Desired luminescence features, high quantum efficiency, strong absorption in blue and near UV spectral region, RGB color purity, high thermal stability of luminescence, high brightness, long-term stability, short emission decay time, low cost and low material usage and environmentally being friendly are the basic requirements for LED phosphors [16, 24-26]. Phosphors are often made from the combination of a crystalline host lattice
and a small amount of certain impurities, the activator ion. Generally, the host matrix should be non-absorbing to the radiation source used for the excitation process. The activator ion absorbs energy and gets excited. The luminescence occurs when this excited activator ion de-excites to the ground state by releasing energy in the form of photons. But in some cases, the exciting radiation is not absorbed by the activator ion. So we need to add another ion in the host lattice called sensitizer. Now the sensitizer ion absorbs the exciting radiation and transfers it to the activator ion. Thus, in the case of phosphor materials luminescence can be achieved by the direct excitation of the activator ion or by the indirect excitation via a sensitizing ion. The proper choice of host lattice and activator ions is essential to obtain an efficient phosphor material. The important applications of phosphor materials include lighting applications, cathode ray tubes, scintillators, vacuum fluorescent displays and field emission displays, electroluminescent materials, plasma display panels, organic fluorescent pigments, luminous paints etc. [1, 16, 27-28].

The activator ions used in the phosphor materials can be transition metals or rare earth ions. Rare earth doped phosphor materials have very important role in optoelectronics and are widely used in solid state lighting applications [28-31]. The rare earth doped phosphors have high efficiency and color tunability, which can be varied by doping different rare earth ions with different compositions [28].

1.3 Host Materials

A large number of phosphor materials are available for the applications of white LEDs. Oxides, nitrides, oxynitrides, sulfides, fluorides, phosphates, selenides, aluminates, silicates and orthosilicates are
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The most commonly used phosphor host materials. Some of the examples for phosphor host materials are YVO₄, CaWO₄, SrCaMoO₄, CaTiO₃, GaN, Sr₂Si₅N₈, ZnS, (Sr₃M)₄F (M= Ca, Sr, B), BaMgAl₁₆O₁₇, (Sr, Mg)₃(PO₄)₂, SrSSe, M₃SiO₅ and M₂SiO₄ (M = Ca, Sr, Ba), etc. [1, 16, 24, 32-35]. The main requirements for the host lattice of phosphors include chemical stability, strong covalent chemical bonds and large crystal field splitting [16]. Among the above mentioned host materials, oxides have high chemical and thermal stability which is suitable for a high efficient phosphor [16].

1.3.1 Sr₀.₅Ca₀.₅TiO₃

Oxide based host materials have widely used in the phosphor applications due to their chemical stability and ease of synthesis [16, 34-35]. Among oxide phosphors, titanates show high chemical, thermal and mechanical stability. Titanates are the compound containing titanium, oxygen and, at least, one additional metallic element. Titanates with general formula, ATiO₃ (A= alkaline earth ions like Ba, Sr, Ca, Mg) are known for their outstanding dielectric, ferroelectric and pyroelectric properties. They have many applications in the fields of capacitor, tunable microwave devices, dynamic random access memories and infrared imaging devices [36-38]. Strontium titanate, barium titanate and calcium titanate are the most common examples of perovskite titanate oxides. Also, the perovskite titanate matrices show dramatic changes in their chemical and physical properties as a result of the structural phase transitions. So they found potential application in the field of optoelectronic devices [39-40]. Rare earth ions doped titanates got much importance because of their high chemical stability and promising luminescence properties like
enhancement of the fluorescence intensity of the desired wavelength with better chromaticity coordinates [41].

Among perovskite structures, Sr$_{1-x}$Ca$_x$TiO$_3$ binary system has attracted much interest for the structural and phase transitions depending on the composition (Ca/Sr ratio) and the preparation temperature [42-44] and is represented in Fig.1.3. C. J. Ball et al. reported the composition dependent phase transition sequence of Sr$_{1-x}$Ca$_x$TiO$_3$ from cubic Pm$ar{3}$m ($x \leq 0.05$), tetragonal I4/mcm ($0.1 \leq x \leq 0.35$), orthorhombic Bmmb ($0.4 \leq x \leq 0.55$) to orthorhombic Pnma ($0.6 \leq x \leq 1$) [44]. However, Ranson P et al. observed four different types of orthorhombic phases in addition to the high temperature cubic Pm$ar{3}$m and tetragonal I4/mcm phase with $0 \leq x \leq 1$ [45]. But T. Yamanaka et al. reported that for $0.4 \leq x \leq 1$, Sr$_{1-x}$Ca$_x$TiO$_3$ shows orthorhombic structure in the Pbnm space group [46]. Depending on the preparation temperature the structure of Sr$_{1-x}$Ca$_x$TiO$_3$ also changes [42-43]. At low temperature the system shows orthorhombic structure (Pbnm and
Bnmb) and transforms to cubic (Pm\text{3}m) structure at high temperature through an intermediate tetragonal (I4/mcm) structure due to the rotations of TiO$_6$ octahedra [45]. Sr$_{1-x}$Ca$_x$TiO$_3$ also undergoes ferroelectric or antiferroelectric phase transition depending on its exact chemical composition [47]. M. Yuanbing et al. reported that the variation in x affects not only on the phases of Sr$_{1-x}$Ca$_x$TiO$_3$ but also on its dielectric constant [26]. The solid solutions of Sr$_{1-x}$Ca$_x$TiO$_3$ have high dielectric constants [48-49]. So they are suitable for microwave device applications [50-51]. A large number of works have been reported on the structural, morphological, thermochemical, dielectric, anti-ferroelectric, ferroelectric, paraelectric and Raman scattering studies of Sr$_{1-x}$Ca$_x$TiO$_3$ (0 ≤ x ≤ 1) [47, 52-60]. For x = 0.5, Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ exhibits orthorhombic structure in the Pbnm space group [45-46]. In the present work spectroscopic and dielectric properties of Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ doped with RE$^{3+}$ (Pr$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$) ions were investigated.

1.4 Rare Earth elements

The rare earth elements mainly include 17 elements consisting of the 15 lanthanides from Lanthanum to Lutetium, Scandium and Yttrium. The electronic configuration of a lanthanide ion can be written as follows:

1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 3d$^{10}$ 4s$^2$ 4p$^6$ 4d$^{10}$ 5s$^2$ 5p$^6$ 6s$^2$ where n is an integer from 2 to 14.

The partially filled 4f electronic energy levels of lanthanide ions are characteristic of each ion. The levels are not affected much by the environment because 4f electrons are well shielded from external electric fields by the outer 5s$^2$ and 5p$^6$ electrons. This feature is in strong contrast with transition metal ions, whose 3d elements located in an outer orbit, is heavily affected by the environmental or crystal electric field. When incorporated in crystalline or amorphous host materials, the rare earth ions
exist as +3 or +2 ions. The triply charged rare earth ions exhibit narrow band intra 4f luminescence in a wide variety of host materials. Also some of the RE ions, like Eu$^{3+}$ and Sm$^{2+}$, exhibit luminescence. Because of the shielding of 4f electrons, the positions of the rare earth electronic levels are much more influenced by spin-orbit interactions than by the applied crystal field. The characteristic energy levels of 4f electrons of trivalent lanthanide ions have been thoroughly investigated by Dieke and his co-workers and are known as Dieke diagram as in Fig.1.4 [61]. The Dieke diagram is applicable to RE$^{3+}$ ions in almost any environment because the maximum variation of the energy levels is, at most, of the order of several hundred cm$^{-1}$. There are mainly two mechanisms for light emission in RE doped phosphor materials. They are 4f - 4f transitions and 4f - 5d transitions.

**4f - 4f transitions:** In the case of 4f - 4f transitions electrons are transferred between different energy levels of the 4f orbitals of the same rare earth ion. But these transitions are forbidden since the parity selection rule says that electronic transitions between energy levels with same parity cannot occur [62]. But their 4f - 4f transitions can occur because the parity selection rule is relaxed due to a perturbation such as electron-vibration coupling and uneven crystal field effect from the host lattice [16]. In the case of rare earth ions the 4f electrons are shielded from the external fields by 5s and 5p electrons, so the crystal field effect from the host is very small. Thus, RE$^{3+}$ ion is uniquely characterized by its energy levels, relatively independent of host matrices. So RE$^{3+}$ ions show narrow f – f absorption and emission.

**4f – 5d transitions:** There are a number of RE$^{3+}$ ions like Ce$^{3+}$, Pr$^{3+}$, Tb$^{3+}$, Er$^{3+}$ and Eu$^{3+}$ emit through an intra-band 4f – 4f transitions or a 5d – 4f transitions. The 4f to 5d transitions are dipole allowed and unlike the 4f
state, the 5d states can diffuse and overlap with ligand orbitals. This is due to the strong dependence of $4f - 5d$ transition in the host material. Thus, with increasing host crystal field the emission will change from line emission in the UV region to band emission in the visible region. For the present work, we have used Pr$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$ as activator ions in the host material. Their importance and general characteristics are given in the next section.

![Energy levels of trivalent rare earth ions](Image Credit: R. C. Ropp 2004).
1.4.1 Praseodymium

Praseodymium is a soft, silvery and ductile metal in the lanthanide group with atomic number 59. In 1841 Mosander extracted the rare earth didymia from lanthana: later in 1885, von Welsbach separated didymia into two others- praseodymium and neodymium. The electronic configuration of praseodymium ion is \([\text{Xe}] 4f^3 6s^2\) \((\text{[Xe]} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6)\). In its compounds praseodymium occurs mainly in three oxidation states, +2, +3 and +4. The ionic radius of \(\text{Pr}^{3+}\) ion is 113 pm. Among lanthanides \(\text{Pr}^{3+}\) has important luminescence characteristics; it shows emission in the blue, green and red region depending on the local environment [63]. Also, they produce infrared emission too. \(\text{Pr}^{3+}\) produces intense emission lines originating from three different levels, namely \(^3\text{P}_0\), \(^1\text{D}_2\) and \(^1\text{G}_4\)[64-65].

1.4.2 Samarium

Samarium is a moderately hard silvery metal with atomic number 62. In 1879, Lecoq de Boisbaudran isolated samarium from didymia obtained from the mineral samarskite. The electronic configuration of samarium ion is \([\text{Xe}] 4f^6 6s^2\). Samarium is one of the lanthanides that exhibit +2 oxidation states, in addition to the +3 oxidation state. The ionic radius of \(\text{Sm}^{3+}\) ion is 109 pm. \(\text{Sm}^{3+}\) ion produces intense orange emission. In the case of \(\text{Sm}^{3+}\) ions the host crystal lattices have little effect on the emission and excitation spectra because of its characteristic \(f - f\) transitions. The \(\text{Sm}^{3+}\) ion is a potential activator for use in warm-white light emitting diodes. It offers high luminous efficacy due to the narrow emission bands. The emission transitions originate from \(^4\text{G}_{5/2}\), \(^4\text{F}_3/2\) and \(^4\text{G}_{7/2}\).
1.4.3 Dysprosium

Dysprosium is a rare earth element with metallic silver luster. The atomic number of dysprosium is 66 with electronic configuration [Xe] 4f¹⁰ 6s². Dysprosium was first identified in 1886 by Paul Emile Lecoq de Boisbaudran. Soluble dysprosium salts are mildly toxic, but the insoluble salts are non-toxic. Like samarium ions, dysprosium ions also exhibit +2 and +3 oxidation states. The ionic radius of Dy³⁺ ion is 105 pm. Dysprosium is fairly stable at room temperature. The Dy³⁺ ion has two intense emission bands in the blue (470-500 nm) and yellow (560-600 nm) regions. It is possible to obtain white light from Dy³⁺ doped phosphors by adjusting the yellow to blue emission intensity ratio and choosing different hosts.

1.5 Synthesis Techniques of phosphor material

In recent years, there have been significant advances in the chemical synthesis of advanced phosphor and ceramic materials for a wide variety of applications. There are a number of methods used to synthesize the phosphor materials like sol-gel method, wet chemical method, solid state reaction method, co-precipitation method, hydrothermal synthesis, solvothermal synthesis, spray pyrolysis, combustion method and polymer precursor method [16, 24, 66]. But the solid state reaction technique is the most commonly used method for the preparation of polycrystalline materials. The high temperature solid state reaction method is straightforward and suitable for mass production.

1.5.1 Solid state reaction method

For the preparation of polycrystalline phosphor materials, the high temperature solid state reaction method is commonly used. This method uses the mixture of solid starting materials, not any solvents. At room
temperature, the solid mixture does not react each other. They will react only at high temperatures, often at 1000 °C - 1500 °C. The reaction conditions, starting materials and their structural properties, the surface area of the solids, their reactivity, thermodynamics of the reaction etc are the factors affecting the feasibility of a solid state reaction technique [67].

Initially, the stoichiometric amount of the solid reactants were weighed and mixed. The natural mixing of the solid reactants is done by using agate mortar and pestle. The fine mixing process will help to improve the reaction rate of the reactants. It is necessary to choose a suitable container which is chemically inert and can withstand high temperatures. Usually, platinum or gold crucibles were used for this purpose. Then the mixture taken in the platinum/gold crucible is fired at an appropriately high temperature. The product obtained is crushed and finely ground for further characterizations.

The advantages of solid state reaction technique include low production cost, produces more amount of products, environmentally friendly, no need for purification steps since there are no solvents used etc. But there are some disadvantages also for solid state reaction method, which include less homogeneity of the product and the presence of defects/impurities.

1.6 Characterization Techniques

The properties of the prepared phosphor materials were analyzed using different characterization techniques. The structural characterization was done using XRD and FTIR analysis. The surface morphology and compositional characterization were done by using SEM and EDS measurements. The optical characterization was carried out by using UV-
Vis-NIR spectroscopy, photoluminescence emission and excitation, decay measurements and dielectric spectroscopy. A brief discussion on the characterization techniques was given in the next sections.

### 1.6.1 X-Ray Diffraction Analysis:

X-Ray diffraction is a very powerful analytical technique used to investigate the structural properties of crystalline materials. Phase identification, grain size determination, lattice constants, unit cell determination, the degree of crystallinity of a mixture etc. can also be determined using XRD pattern. XRD analysis is based on the constructive interference of monochromatic x-rays and a crystalline sample when the Bragg’s law is satisfied \[ n\lambda = 2d\sin\theta \] \hspace{1cm} (1.1)

where \( n \) is a positive integer, \( \lambda \) is the wavelength of the incident wave, \( \theta \) is the diffraction angle and \( d \) is the lattice spacing. The X-ray diffraction pattern is produced when a material is irradiated with a collimated beam of x-rays. In an XRD spectrum, the intensity of the diffracted x-ray is measured as a function of diffraction angle \( 2\theta \). The quantitative identification is carried out by comparing the XRD spectrum of an unknown material with the internationally recognized ICDD (International Center for Diffraction Data) database. There is a unique X-ray diffraction pattern for every crystalline material.

The average crystallite size of prepared samples was calculated from the most intense XRD peak using the Debye-Scherrer formula \[ D = \frac{k\lambda}{\beta\cos\theta} \] \hspace{1cm} (1.2)

where \( k = 0.89 \), \( \lambda \) is the wavelength of Cu-K\( \alpha \) radiation in nanometres, \( \theta \) is the Bragg angle of X-ray diffraction peak and \( \beta \) is the full width at half
maximum (FWHM) of the diffraction peak. The crystalline structure of the prepared phosphors was obtained using a PANalytical X’Pert Pro Diffractometer with Cu-Kα radiation at \( \lambda = 1.5406 \) Å, with an applied voltage of 45kV and 30 mA anode current.

**1.6.2 Fourier Transform Infrared Spectroscopy:**

Fourier Transform Infrared Spectroscopy is a technique used to provide information about chemical bonding or molecular structure of the materials. It is used to identify unknown materials including organic or inorganic compounds. Generally infrared light can be categorized as far infrared (4-400 cm), mid-infrared (400-4000 cm) and near-infrared (4000-140000 cm). Interaction with infrared light causes molecules to undergo vibrational transitions, such as the chemical bond will stretch, bend and contract. As a result, a chemical functional group tends to absorb infrared radiation in a specific wavenumber range. By correlating the band position with the chemical structure, will help to identify a functional group present in a material. The wavenumber positions where functional group absorbs IR radiation are independent of temperature, pressure or change in the molecular structure in other parts of the molecule.

**1.6.3 Scanning Electron Microscopy:**

The scanning electron microscopy is mainly used to understand the surface morphology of the phosphor materials. In scanning electron microscopy, the electron beam interacts with the sample and creates various signals such as secondary electrons, internal currents, photon emission etc. These signals can be appropriately detected and is highly localized to the area directly under the beam. These signals were used to modulate the brightness of a cathode ray tube, which is raster scanned in
synchronism with the electron beam, an image is formed on the screen. This image is highly magnified and has a much greater depth of field. Thus, the SEM images will provide a highly magnified image of the surface of the material along the composition near the surface regions. The scanning electron microscope (SEM) measurements of the prepared samples were carried out by using a JEOL JSM-6390LV.

1.6.4 Energy Dispersive X-ray Spectra:

The energy dispersive X-ray spectrum (EDS) is used to confirm the chemical composition of the prepared samples. In EDS spectroscopy, an energy dispersive detector is used to separate the characteristic X-rays of different elements into an energy spectrum and the inbuilt EDS system software analyzes the energy spectrum to determine the abundance of the specific elements. Generally, EDS instruments are integrated into either a SEM or TEM instrument. EDS system includes a sensitive X-ray detector, a liquid nitrogen dewar for cooling and a software to collect and analyze the obtained energy spectra. At the end of the long arm of the sample chamber of the main instrument, the detector is mounted and is cooled by using liquid nitrogen. Usually, the detectors are made of Si (or Li) crystals that operate at low voltages. This crystal detector absorbs the energy of incoming X-rays by ionization. The free electrons in the crystals become conductive and produce electric charge bias. Thus, the absorbed X-rays are converted to electric voltages of proportional size ie. the electric pulses corresponding to the characteristic X-rays of the elements. Swift EDOXFORD instrument along with the SEM apparatus JEOL JSM-6390LV was used to get the energy dispersive X-ray spectra.
1.6.5 UV-Visible-NIR Spectroscopy

The absorption studies in UV-visible-NIR region are widely used for the quantitative and qualitative determination of the ions present in the sample. The shorter wavelength, high energy radiation in the UV (200-400 nm) and visible (400-700 nm) range of electromagnetic spectrum causes materials to undergo electronic transitions. When the energy from UV or visible light is absorbed by a molecule, its electrons jump from a lower energy level to a higher energy molecular orbital. Varian Cary 5000 UV-Vis-NIR spectrophotometer is used to record the absorption spectra of the samples. The spectrum obtained is a plot of wavelength versus absorbance. The peaks in the absorption spectra correspond to the wavelength of radiation whose energy is equal to that required for an electronic transition.

1.6.6 Photoluminescence Emission (PL) and Excitation (PLE) Spectroscopy

Photoluminescence is the spontaneous emission of photons from a material under optical excitation. The material absorbs radiation of certain wavelength and re-emits photons with a different wavelength. Under optical excitation, the electrons in the material absorb energy and move to the excited state. By releasing the excess energy the electron in the excited state return to the stable ground state. The excess energy can be radiative or non-radiative. The radiative emission of excess energy is termed as photoluminescence and is related to the difference in the energy levels between the two electronic states. In photoluminescence spectroscopy, the excitation energy is fixed to analyze the luminescence properties.

The photoluminescence excitation is also used to study the interaction of electromagnetic radiation with matter. Here the emission wavelength is fixed and the excitation intensity is measured corresponding
to different wavelengths. The peaks in the excitation spectra correspond to the absorption lines of the material. It is a useful method to investigate the electronic level structure of the materials with low absorption, because of the superior signal to noise ratio compared to absorption spectroscopy.

The photoluminescence emission and excitation measurements were carried out by using Horiba Jobin-Yvon Fluoromax-4 at room temperature. It contains a xenon arc lamp, emission and excitation monochromators, a photomultiplier tube (PMT) for signal detection and a reference photodiode.

1.6.7 Optical spectral characterizations

1.6.7.1 Optical band gap energy

The absorption coefficient ‘$\alpha$’ is related to the photon energy ‘$h\nu$’ and the band gap energy ‘$E_g$’ by Mott’s relation

$$\alpha = \alpha_0 \left( h\nu - E_g \right)^n$$  \hspace{1cm} (1.3)

where $\alpha_0 = \frac{A}{h\nu}$. Therefore Eqn.1.3 becomes

$$\alpha = \frac{A}{h\nu} \left( h\nu - E_g \right)^n$$

$$\left( h\nu \right)^n = A \left( h\nu - E_g \right)^n$$  \hspace{1cm} (1.4)

where $n = \frac{1}{2}$ for direct allowed, $n = 2$ for indirect allowed, $n = \frac{3}{2}$ for direct forbidden and $n = 3$ for indirect forbidden. Most of the titanate perovskite have band gap energy value more than or nearly equal to 3 eV [70]. Generally perovskite structures have direct allowed transitions. Thus $n = \frac{1}{2}$ and Eqn.1.4 becomes
\[(\alpha h\nu)^2 = A^2 (h\nu - E_g)\]  
\[(1.5)\]

when \(\alpha = 0\), the value of photon energy \((h\nu)\) will give the band gap energy.

### 1.6.7.2 Nephelauxetic ratio and bonding parameter

The nature of RE\(^{3+}\) ligand bond in a material can be understood by evaluating the nephelauxetic ratio \((\beta)\) and bonding parameter \((\delta)\) [71]. The nephelauxetic ratio is given by the equation

\[\beta = \frac{v_c}{v_a}\]  
\[(1.6)\]

where \(v_c\) and \(v_a\) are the energies in cm\(^{-1}\) for a particular transition in the present host and aqueous solution respectively. The bonding parameter is given by the equation

\[\delta = \frac{1-\beta'}{\beta'} \times 100\]  
\[(1.7)\]

where \(\beta'\) represents the average of the nephelauxetic ratios for all the observed transitions in the absorption spectrum. Depending on the positive or negative sign of the bonding parameter, the RE\(^{3+}\) ligand bond can be covalent or ionic respectively.

### 1.6.7.3 Judd-Ofelt intensity parameters

The spectroscopic studies using Judd-Ofelt (JO) analysis is an important step for the better understanding of different optical properties like transition probabilities and oscillator strengths of various transitions between energy levels of RE ions in different luminescent materials. Unfortunately, these are extremely difficult to measure but can be calculated using JO theory [72-73]. The experimental oscillator strength [74]
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of the absorption transition from the ground state to an excited state was found by integrating the absorbance for each transition using the equation

\[ f_{exp} = 4.32 \times 10^{-9} \int \varepsilon(\nu) d\nu \]  

(1.8)

where \( \varepsilon(\nu) \) is the molar absorption coefficient of an absorption band at a wavenumber \( \nu \) (cm\(^{-1}\)) and \( d\nu \) is the half-band width.

In JO theory the calculated oscillator strength [72-73] of an absorption transition from the ground state \( \Psi J \) to an excited state \( \Psi J' \) can be expressed by the equation

\[ f_{cal} = \frac{8\pi^2 m v^2 (n^2 + 2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_{\lambda} | < \Psi J | U^{(\lambda)} | \Psi J' > |^2 \]  

(1.9)

where \( m \) represents the mass of an electron, \( h \) is the Planck’s constant, \( v \) is the mean energy of the transition, \( J \) is the total angular momentum of the initial state, \( \Omega_{\lambda} \) is the JO intensity parameters \( (\Omega_2, \Omega_4, \Omega_6) \) and \( \| U^{(\lambda)} \|^2 \) is the doubly reduced matrix elements of unit tensor operator evaluated in the intermediate coupling approximation for the absorption transition [75]. \( n \) is the refractive index of the material. The least square fitting of Eqn.1.9 was used to calculate the JO intensity parameters.

The standard JO theory assumes the energy difference between 4f and 5s orbitals is very large and the 5d orbitals do not affect the f-f transition intensities. But in the case of Pr\(^3+\) ions, the energy difference between 4f and 5d orbitals is small (~15000 cm\(^{-1}\)) and influences the f-f transition intensities. The modified JO theory proposed by Kornienko et al. [76] consider the small energy difference between 4f and 5d orbitals by introducing an extra fitting parameter \( (\alpha) \). The modified JO theory gives
reasonably good agreement between the experimental and calculated oscillator strengths with less rms deviation, even after including the hypersensitive transition [76]. According to modified JO theory the oscillator strength for the electric dipole transitions are calculated by

\[
f_{\text{cal}} = \frac{8\pi^2mcv}{3n(2J+1)} \cdot \frac{(n^2 + 2)^2}{9n} \cdot \sum_{\lambda=2A,6} \Omega_{\lambda} \left[ 1 + 2\alpha(E_j + E_j') - 2E_{p\rho} \right] | < \Psi_j < \| \Omega^{(1)} \| \Psi_j' > |^2
\]  

(1.10)

where \( E_j \) is the ground state energy, \( E_j' \) is the excited state energy, \( E_{p\rho} \) is the energy of the center of gravity of the 4f configuration (-9940 cm\(^{-1}\)) and \( \alpha = \frac{1}{2} \left[ E(4f - 5d) - E(4f) \right] \). The parameter \( \alpha \) is the additional fitting parameter and has a value of 10\(^{-6}\) cm\(^{-1}\) [75]. The quantity of best fit between experimental and calculated oscillator strengths can be expressed by the root mean square of oscillator strengths (\( \sigma \)) and is given by

\[
\sigma = \left[ \frac{\sum(f_{\text{exp}} - f_{\text{cal}})^2}{N_i} \right]^{1/2}
\]  

(1.11)

where \( N_i \) represents the total number of excited energy levels used for least square fit. Using JO parameters we can also calculate the spectroscopic quality factor [77] and is represented by the equation

\[
\chi = \frac{\Omega_{A}}{\Omega_{6}}
\]  

(1.12)

### 1.6.7.4 Radiative Properties

The radiative parameters can be found by combining the JO intensity parameters obtained from the absorption data with the experimental photoluminescence spectra. The radiative transition probability for a transition from the ground state to excited state, \( \Psi_j \rightarrow \Psi_j' \) is the sum of electric and magnetic-dipole transitions probabilities [72-73] and is given by J-O theory as
\[ A(\Psi J, \Psi' J') = A_{ed} + A_{md} = \frac{64\pi^4}{3h\lambda^3(2J+1)} \times \left( \frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right) \]  
\text{(1.13)}

where \( S_{ed} \) and \( S_{md} \) represent the electric and magnetic-dipole transition line strengths, respectively and is given by the expressions

\[ S_{ed} = e^2 \sum_{J=2,4,6} \Omega_J | \langle \Psi J | U^{(J)} | \Psi' J' \rangle |^2 \]  
\text{(1.14)}

and

\[ S_{md} = \frac{e^2 h^2}{16\pi^2 m^2 c^2} | \langle \Psi J | L + 2S | \Psi' J' \rangle |^2 \]  
\text{(1.15)}

\( n(n^2+2)^2/9 \) and \( n^3 \) in Eqn. 1.13 are the local field corrections for electric and magnetic dipole transition respectively. So the total radiative transition probability \( A_R(\Psi J) \) can be expressed as

\[ A_R(\Psi J) = \sum_{\Psi' J'} A(\Psi J, \Psi' J') \]  
\text{(1.16)}

The predicted radiative lifetime \( (\tau_R) \) and the fluorescence branching ratio, \( \beta_R(\Psi J, \Psi' J') \) from the ground state \( \Psi J \) to an excited state \( \Psi' J' \) can be calculated by using the following equations respectively.

\[ \tau_R = [A_R(\Psi J)]^{-1} \]  
\text{(1.17)}

\[ \beta_R(\Psi J, \Psi' J') = \frac{A(\Psi J, \Psi' J')}{A_R(\Psi J)} \]  
\text{(1.18)}

To identify the potential emission transitions of rare earth ions in a host matrix we have to calculate the value of stimulated emission cross-section \( (\sigma_e) \). The stimulated emission cross section \( (\sigma_e) \) for a particular transition can be calculated by

\[ \sigma_e = \frac{\lambda_p^4 A(\Psi J, \Psi' J')}{8\pi c n^2 \Delta \lambda_{eff}} \]  
\text{(1.19)}

where \( \Delta \lambda_{eff} \), \( \lambda_p \) and \( c \) are the full width at half maximum of the transition, the peak wavelength of emission band and the velocity of light respectively. Also the value of gain bandwidth \( (\sigma_e \times \Delta \lambda_{eff}) \) and optical gain \( (\sigma_e \times \tau_R) \) are very important to predict the amplification of the medium in which the rare earth ions were incorporated.
1.6.7.5 Luminescence decay analysis

At lower concentration, the interaction between RE$^{3+}$ ions are negligible and the normal single exponential function,

$$I(t) = I_0 + Ae^{-t/\tau}$$  \hspace{1cm} (1.20)

was used to fit decay curves, where $I_0$ is the initial intensity, $I(t)$ is the intensity at time $t$, $A$ is the pre-exponential factor and $\tau$ are the lifetime. As the concentration of RE$^{3+}$ ions increases the contribution of energy transfer to the lifetime becomes highly significant and the decay curves show non-exponential behaviour [78]. So the decay curve was fitted by non-exponential function expressed as

$$\tau = \int \frac{t I(t) dt}{\int I(t) dt}$$  \hspace{1cm} (1.21)

where $I(t)$ is the emission intensity at time $t$. The decay curves at higher concentration can also be well fitted by using a biexponential function [79],

$$I(t) = A_f e^{-t/\tau_f} + A_s e^{-t/\tau_s}$$  \hspace{1cm} (1.22)

where $\tau_f$ and $\tau_s$ are the fast and slow decay times and $A_f$ and $A_s$ are their respective weight factors. The average lifetime can be expressed as

$$\bar{\tau} = \frac{A_f \tau_f^2 + A_s \tau_s^2}{A_f \tau_f + A_s \tau_s}$$  \hspace{1cm} (1.23)

In some cases the experimental lifetime ($\tau_{exp}$) of RE$^{3+}$ ion is considerably smaller than the predicted lifetime ($\tau_R$) obtained through JO analysis. This radical change in lifetimes may be due to the energy transfer through cross-relaxation between the RE$^{3+}$ ions [80]. So we can express the non-radiative energy transfer rate in terms of experimental ($\tau_{exp}$) and radiative ($\tau_R$) lifetimes. The non-radiative energy transfer rate [81] is given by

$$W_{NR} = \frac{1}{\tau_{exp}} = \frac{1}{\tau_R}$$  \hspace{1cm} (1.24)
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The quantum efficiency ($\eta$) of the emission transition is equal to the ratio of the measured lifetime to the predicted lifetime and is given by

$$\eta = \frac{\tau_{\text{exp}}}{\tau_{\text{R}}} \times 100$$

(1.25)

Using the experimental lifetime we can calculate the gain coefficient ($g$) by the equation

$$g = \tau_{\text{exp}} \times \sigma_e(\lambda_p)$$

(1.26)

where $\tau_{\text{exp}}$ is the experimental lifetime and $\sigma_e$ is the stimulated emission cross-section at the wavelength $\lambda_p$.

### 1.6.7.6 Colorimetric Analysis

In 1931, the Commission Internationale de l’Eclairage developed an international standard to identify/represent all visible colors, called CIE color coordinates [82]. Using chromaticity diagram one can identify any color in terms of CIE color coordinates. The CIE color system offers more precision in color measurements since the parameters are based on the spectral power distribution of the light emitted from a material and are factored by sensitivity curves which have been measured from the human eye. The response of the human eye to the visible spectrum is described in terms of tristimulus values ($X$, $Y$ & $Z$). They are the amounts of the three primary colors in a three component additive color model. The tristimulus values for a color with spectral distribution $I(\lambda)$ can be calculated using the CIE color matching functions $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$.

$$X = \int_0^\infty I(\lambda) \bar{x}(\lambda) d\lambda$$

(1.27)

$$Y = \int_0^\infty I(\lambda) \bar{y}(\lambda) d\lambda$$

(1.28)
where the integration limits are the entire visible spectrum in the emission spectrum and $I(\lambda)$ is the emission spectrum of the sample. The tristimulus values X, Y and Z specify a color’s lightness (light or dark), hue (red, orange, yellow, green, blue, purple) and saturation (pink-red, pastel-fluorescent, baby blue-deep blue) [10]. Using these tristimulus values we can calculate the CIE color coordinates as:

\[
x = \frac{X}{X + Y + Z}, \quad y = \frac{Y}{X + Y + Z}, \quad z = \frac{Z}{X + Y + Z}.
\]

where $x + y + z = 1$: only two of the color coordinates are independent and can construct the chromaticity diagram using $x$ and $y$. The plot of CIE $y$ coordinates versus CIE $x$ coordinates is a horse-shoe shaped diagram, known as the CIE chromaticity diagram, as in Figure 1.3. The CIE
coordinates corresponding to the standard red, green, blue and white are (0.65, 0.35), (0.3, 0.6), (0.15, 0.1) and (0.33, 0.33) respectively.

Using CIE color coordinates we can calculate the correlated color temperature (CCT) and color purity of the phosphor samples. The correlated color temperature using McCamy’s approximate formula [83] is given by

\[ \text{CCT} = -449 n^3 + 3525 n^2 - 6823.3 n + 5520.33 \]

(1.30)

where \( n = \frac{x - x_e}{y - y_e} \), \((x, y)\) is the CIE color coordinates and \((x_e = 0.3320, y_e = 0.1858)\) is the epicentre of the convergence. The color purity is the weighted average of the \((x, y)\) coordinate relative to the coordinate of the illuminant C \((0.3101, 0.3162)\) and the coordinate of the dominant wavelength, and is given by the equation [84]

\[ \text{color purity} = \frac{\sqrt{(x_s - x_i)^2 + (y_s - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100 \% \]

(1.31)

where \((x_s, y_s)\) and \((x_i, y_i)\) represents the CIE coordinates corresponding to the sample point and illuminant point respectively. \((x_d, y_d)\) is the coordinates corresponding to the dominant wavelength. The dominant wavelength is the single monochromatic wavelength of the spectrum whose chromaticity coordinates is on the same straight line as the sample point and illuminant point.

1.6.8 Dielectric spectroscopy

Dielectric spectroscopy (Impedance spectroscopy), also known as electrochemical impedance spectroscopy, is an efficient way to study the electrical properties of materials. Complex impedance, alternating current (AC) conductivity and dielectric relaxation can be studied by using dielectric spectroscopy. On the basis of the variation of the dielectric
constant, dielectric loss and AC conductivity in a wide range of frequencies, we can get information about the insulating and conduction characteristics of a material [85]. To check the device performance, it is necessary to know the values of dielectric constant and dielectric loss. Dielectric materials with the low dielectric loss, high tunability and suitable dielectric constant are required for microwave applications [86]. The defects in the amorphous semiconductor materials can also be studied by measuring the AC conductivity of the samples. Electrochemical impedance spectroscopy has been quite well known for its applications in the solid electrolyte conductivity measurements [87]. But it has a wide range of applications also in the paint industry, biosensor systems, food industry, bioelectrical impedance analysis etc. [88-92].

The dielectric spectroscopy is mainly sensitive to the dipolar and localized charged particles in a material. The dielectric materials are mainly insulators. When an electric field is applied to such materials, the electric charges shift from their average equilibrium position causing polarization. The amount of polarization caused can be represented by a dimensionless quantity called dielectric constant. The polarization effect will also be dependent on the nature of the dipole and the frequency of the applied field. This displacement due to polarization may persist even when the field is ceased of. This gives rise to decay time to attain the equilibrium and the phenomenon is known as relaxation. The decay time is known as relaxation time, \( \tau \). Electrical characterization of the structure of a material can be analyzed using dielectric spectroscopy. It is based on the interaction of external electric field with the electric dipole moment of a material. The variation of parallel capacitance (\( C_p \)), dissipation factor (\( D \)), impedance (\( Z \))
and phase angle ($\theta$) as a function of frequency will provide the quantitative information about the dielectric constant, conductivity, impedance etc. We can also represent these parameters as a function of temperature also. The plot between real and imaginary part of impedance (Cole-Cole plot) has been used to determine the molecular relaxation time, $\tau$. It appears in the form of a semi-circle. Formation of full, partial or no semicircles mainly depends on the strength of relaxation [93]. Small poorly resolved semicircles can be associated with ionic transfer from either the atmosphere or electrodes with the ceramic. Bulk Capacitance ($C_b$) and bulk resistance ($R_b$) can also be found from the Cole-Cole plot. Thus for single semicircles showing single relaxation time we can model by an equivalent parallel RC circuit. The AC conductivity and dielectric measurements were carried out by using a dielectric relaxation spectrometer, Agilent E4980A, in the frequency range 100 Hz – 2 MHz.

Using these characterization methods different properties of the prepared phosphor samples were analyzed and discussed in the coming chapters.

1.7 The Proposed Research Work

1.7.1 Main Goal

Preparation of Pr$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ phosphors by solid state reaction method to study its luminescent and dielectric properties.

1.7.2 Specific Goals

✓ Preparation of Pr$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ reddish-orange phosphors and it's spectroscopic and luminescent characterization.
✓ Preparation and spectroscopic characterization of Sm$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ yellow emitting phosphors.
✓ Spectroscopic and photoluminescence characterization of UV excited Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ phosphors for white LED applications.
✓ Dielectric and AC conductivity studies of Sr$_{0.5}$Ca$_{0.5}$TiO$_3$:x Pr$^{3+}$, Sm$^{3+}$ & Dy$^{3+}$ phosphor samples.

1.7.3 Organization of the Work

Chapter II presents the luminescence characteristics and modified Judd-Ofelt analysis of UV excited Sr$_{0.5}$Ca$_{0.5}$TiO$_3$:x Pr$^{3+}$ reddish-orange phosphors. Chapter III describes the spectroscopic and luminescence properties of Sr$_{0.5}$Ca$_{0.5}$TiO$_3$:x Sm$^{3+}$ yellowish orange emitting phosphors. The spectroscopic characterization of UV excited Sr$_{0.5}$Ca$_{0.5}$TiO$_3$:x Dy$^{3+}$ white light emitting phosphors is reported in Chapter IV. Chapter V explains the dielectric and AC conductivity studies of undoped and different concentrations of Pr$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$ doped Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ samples at room temperature. All the phosphor samples were prepared by using solid state reaction technique. Chapter VI summarizes overall conclusions and future scope of the present work.

1.8 Conclusions

A brief history of lighting devices, the importance of phosphor materials and its applications are discussed in this chapter. Important characteristics of host matrix and activator ions used in the present work are also discussed. Details of the various type of characterization techniques, like XRD, EDS, SEM, FTIR, UV-Vis-NIR spectroscopy, photoluminescence emission and excitation, decay measurements and dielectric spectroscopy, used for the prepared phosphor materials are also
included in this chapter. The chapter concluded with the main goal and future scope of the present work.
References


